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(54) **Heat curable primerless silicone hardcoat compositions**

Hitzehärtbare, grundierungslose harte Siloxanüberzugzusammensetzungen

Compositions de revêtement dur en silicone, durcissable à la chaleur et ne nécessitant pas de revêtement de fond

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(56) References cited:
EP-A- 0 306 700
DE-A- 3 323 911

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Description

The present invention relates to primerless silicone hardcoat compositions comprising an aqueous/organic solvent silicone dispersion consisting essentially of colloidal silica, and a partial condensate of an organoalkoxysilane, in combination with an effective amount of an adhesion promoter in the form of a caprolactone based polyester polyol.

Prior to the present invention, as shown by Patel, U.S. Patent 5,041,313, silicone hardcoat composites were made by initially priming a thermoplastic substrate, such as a polycarbonate substrate, with a solution of a polyacrylic resin in a solvent blend, followed by the application of a silicone hardcoat composition. European patent application 0439294Al suggests that priming a thermoplastic substrate prior to the application of the silicone hardcoat is not necessary if a monomeric hydroxy acrylate such as 2-hydroxy ethyl methacrylate is added to the hardcoat mixture before it is thermally cured. However, the use of hydroxy acrylates in coating compositions has sometimes been restricted because of their toxicity, as taught in Chung, U.S. Patent 4,486,504.

EP-A-0306700 discloses a coating composition comprising colloidal silica, a partial condensate of an organoalkoxysilane and a copolymer of ethylenically unsaturated monomers.

In copendingapplication EP-A-0570165, it was found that an acrylated or methacrylated polyurethane, or an acrylic polyol copolymer, having $\overline{M}_n$ (number average molecular weight) of at least 1000 could be used as an adhesion promoter in the aqueous/organic solvent silicone dispersion. The term "aqueous/organic solvent silicone dispersion" means a dispersion consisting essentially of colloidal silica and the partial condensate of an organoalkoxysilane as defined in more detail hereinafter. The resulting silicone hardcoat compositions can be applied directly onto a variety of unprimed thermoplastic substrates, such as a polycarbonate substrate, followed by a thermal cure to provide thermoplastic composites exhibiting improved adhesion and weathering resistance.

Summary of the Invention

The present invention is based on the discovery that a caprolactone based polyester polyol, such as a caprolactone based polyester diol or triol, can be used as adhesion promotors for a heat curable colloidal silica filled organopolysiloxane . The resulting heat curable organopolysiloxane composition can be used directly on an unprimed polycarbonate surface to provide an abrasion and weather resistant polycarbonate substrate. The treated polycarbonate substrate also exhibits an excellent cross hatch adhesion value after an extended period of water immersion at 65°C.

Statement of the Invention

There is provided by the present invention, a heat curable primerless silicone hardcoat composition comprising by weight,

(A) 100 parts of an aqueous/organic solvent silicone dispersion having 10-50% by weight of solids and consisting essentially of 10-70% by weight of colloidal silica and 30-90% by weight of a partial condensate of an organoalkoxysilane, and

(B) 1 to 10 parts, and preferably 1 to 5 parts, of a caprolactone based polyester polyol.

Organoalkoxysilanes which can be used in the preparation of the aqueous/organic solvent dispersion of the heat curable primerless silicone hardcoat compositions of the present invention are included within the formula,

$$(R)_aSi(OR^1)_{4-a} \quad (1)$$

where R is a $C_{(1-6)}$ monovalent hydrocarbon radical and preferably a $C_{(1-4)}$ alkyl radical, R^1 is an R or a hydrogen radical and a is a whole number equal to 0 to 2 inclusive. Preferably, the organoalkoxysilane included within formula (1) is methyltrimethoxysilane, methyltrihydroxysilane, or a mixture thereofwhich can form a partial condensate.

Some of the aqueous/organic solvent dispersions of colloidal silica which can be used in the practice of the present invention are shown by Clark, U.S. Patent 3,986,997. These aqueous/organic solvent dispersions can be prepared by adding a trialkoxysilane, such as methyltrimethoxysilane to a commercially available aqueous dispersion of colloidal silica such as Ludox HS of the E.I.duPont de Nemours and Company and Nalco 1034A of the Nalco Chemical Co. of Naperville, IL, which has been treated with glacial acetic acid to adjust the pH. After the addition of the methyltrimethoxysilane, the resulting acidified dispersion is allowed to stand for about 1 hour until the pH is stabilized at about 4.5. The resulting compositions can be aged for several days to insure formation of the partial condensate of methyltri-

methoxysilane and the silica methanol-water dispersion. Another source of a dispersion of colloidal silica is shown by Ubersax, U.S. Patent 4,177,315 which utilizes a colloidal silica dispersion such as Ludox HS resulting from the hydrolysis of tetraethylorthosilicate by the addition of aliphatic alcohol and an acid. One of the preferred aqueous/organic solvent dispersions of colloidal silica can be made by initially mixing methyltrimethoxysilane and acetic acid thereafter adding Ludox, AS-40, the colloidal silica of the aforementioned Ubersax patent along with deionized water. The resulting mixture can then be agitated for 16 hours or more under ambient conditions during which time a suitable alcohol, such as isopropanol or butanol can be added. Additional organotrialkoxysilanes included within formula (1) are for example,

tetraethoxysilane,
ethyltriethoxysilane,
diethyldiethoxysilane,
tetramethoxysilane,
methyltrimethoxysilane, and
dimethyldimethoxysilane.

In the practice of the present invention, the heat curable primerless silicone hardcoat compositions can be made by combining the caprolactone based polyester polyol, or adhesion promoter, with the aqueous/organic solvent silicone dispersion consisting essentially of organoalkoxysilane, colloidal silica and sufficient alcohol. Additional silicone dispersions which can be used with the adhesion promoter are shown by U.S. Patents, 3,986,997, 4,624,870, 4,680,232 and 4,914,143.

UV (ultraviolet light) light absorbing agents which are described by Ashby et al, U.S. Patents 4,278,804, 4,374,674, and 4,419,405, Frye, U.S. Patent 4,299,746 and by Anthony, U.S. Patents 4,495,360 and 4,525,426 can be incorporated. UV absorbers such as those of hydroxy benzophenone and benzotriazole serves as well as the triazine, cyanoacrylates and benzylidene malonates. Other additives such as free radical initiators, hindered amine light stabilizers, antioxidants, dye, flow modifiers and leveling agents or surface lubricants can bs used. Other colloidal metal oxides can be present at up to about 10% by weight of the aqueous/organic solvent dispersion with colloidal silica and include metal oxides such as, antimony oxide, cerium oxide, aluminum oxide and titanium dioxide. Preferred UV absorbers are the ones which coreact with silanes and is less likely to volatalize during the heat cure. Preferred compounds are 4[gamma-(trimethoxysilyl)propoxy]-2,hydroxybenzophenone, 4[gamma-(triethoxysilyl)propoxy-2,hydroxybenzophenone or their mixtrures. UV absorbers can be used as 2 to 20 wt. % level.

Among the caprolactone based polyester polyols are Tone®Polyols, which are commercially available from the Union Carbide Chemicals and Plastic Company, Inc., Danbury Conn. These polyester polyols are provided as difunctional or trifunctional materials. Typical properties are as follows:

Table 1

Difunctional	Average Molecular Weight	Hydroxy No.,mg KOH/g	Melting Point Range,°C	Viscosity at 55°C, CP	Special Gravity, 55/20°C
Tone 0200 Polyol	530	212	30 to 40	88	1.073
Tone 0201 Polyol	530	212	<0 to 40	65	1.072
Tone 0210 Polyol	830	133	35 to 45	167	1.072
Tone 0221 Polyol	1000	112	28 to 40	155	1.072
Tone 2221 Polyol	1000	212	<0 to 22	175	1.072
Tone 0230 Polyol	1250	90	40 to 50	284	1.071
Tone 0240 Polyol	2000	56	45 to 55	635	1.071
Tone 0240 HP Polyol	2000	56	45 to 55	635	1.071
Tone 0241 Polyol	2000	56	43 to 55	444	1.071

de matières solides et constituée essentiellement de 10 à 70% en poids de silice colloïdale et 30 à 90% en poids d'un produit de condensation partielle d'un organoalcoxysilane, et
(B) 1 à 10 parties d'un agent favorisant l'adhérence, constitué essentiellement d'un polyester-polyol à base de caprolactone.

2. Composition à base de silicone, durcissable par la chaleur, pour revêtement dur sans couche primaire, selon la revendication 1, pour laquelle l'organoalcoxysilane est le méthyltriméthoxysilane.

3. Composition à base de silicone, durcissable par la chaleur, pour revêtement dur sans couche primaire, selon la revendication 1, dans laquelle l'agent favorisant l'adhérence est un polycaprolactone-diol.

4. Composition à base de silicone, durcissable par la chaleur, pour revêtement dur sans couche primaire, selon la revendication 1, dans laquelle l'agent favorisant l'adhérence est un polycaprolactone-triol.

5. Composite constitué d'une feuille thermoplastique portant un revêtement durci, résultant du durcissement par la chaleur d'une composition à base de silicone, durcissable par la chaleur, pour revêtement dur sans couche primaire, qui comprend en poids :

(A) 100 parties d'une dispersion dans un mélange d'eau et de solvant organique, contenant 10 à 50% en poids de matières solides, et constituée essentiellement de 10 à 70% en poids de silice colloïdale et 30 à 90% en poids d'un produit de condensation partielle d'un organoalcoxysilane, et
(B) 1 à 10 parties d'un agent favorisant l'adhérence, constitué essentiellement d'un polyester-polyol à base de caprolactone.

6. Composite selon la revendication 5, dans lequel la feuille thermoplastique est une feuille de polycarbonate.